| | | | |
|---|---|---|---|
| Chemical recovery | Most of process is devoted to the recovery of cooking chemicals, with incidental recovery of heat through burning organic matter dissolved in liquor from wood; chemical losses from system are replenished with salt cake, $Na_2SO_4$ | $SO_2$ relief gas recovered; magnesium liquor recovered and reused after wood digestion and pulp washing | Characterized by high yield—65–85%. Pulping losses 35–15% of wood components. Special recovery methods and by-product utilization |
| Materials of construction | Digesters, pipelines, pumps, and tanks can be made of mild steel or, preferably, of stainless | Acid liquor requires digester lining of acid-proof brick; fittings of chrome-nickel steels (Type 316), lead, and bronze | Serious corrosion problems encountered in digesters and handling equipment; stainless-steel protection needed |
| Pulp characteristics | Brown color; difficult to bleach; strong fibers; resistant to mechanical refining | Dull white color; easily bleached; fibers weaker than kraft | Stiff, dense paper of low opacity; fibers approach chemical pulps in strength |
| Typical paper products | Strong brown bag and wrapping, multiwall bags, gumming paper, building paper, strong white paper from bleached kraft, paperboards such as used for cartons, containers, milk bottles, and corrugated board | White grades: book paper, bread wrap, fruit tissue, sanitary tissue | Unbleached: large percentage for corrugated board, also newsprint, specialty boards. Bleached: writing and bond papers, offset, mimeo, tissue, and toweling |

pulp from wood. Some work better on softwood than hardwood, some give high-yield lower-quality papers, some give low-yield superior papers, etc. The major processes are: sulfate or kraft process, groundwood and thermomechanical process, semichemical process, and sulfite process. Considering the variety of wood available, the many uses of paper, and the complexity of the process, it is not surprising that Casey[4] differentiates 5 mechanical processes, 7 chemimechanical and thermomechanical processes, 5 semichemical processes, 3 high-yield chemical processes, 11 full chemical processes, and 2 processes suitable for dissolving (high or chemical) pulp. There are also a host of new processes (solvent, oxygen, catalytic, and enzymatic processing) that have been suggested. Most are technically possible but economically unfeasible. Bearing in mind that many variations are possible, an attempt is made here to describe typical solutions to the problems encountered in processing wood to pulp.

***KRAFT PULPING.*** Kraft, or sulfate, pulping is an alkaline process by which most pulp is presently made. It is an outgrowth of the obsolete soda process which cooked with a strong (12%) solution of NaOH and $Na_2CO_3$. The soda process gave low yields and worked well only with short-fibered hardwoods. The material added to the cooking liquor for the kraft process is $Na_2SO_4$, hence the common name of the sulfate process. The cooking, however, is done with a solution containing $Na_2S$, NaOH, and $Na_2CO_3$ formed from the sulfate during preparation and recovery of the cooking liquor. Although all sorts of woods can be cooked by the kraft process and the fibers obtained are bleachable and strong, it is very important that the chemicals used can be recycled and regenerated, reducing or even eliminating stream pollution. Odoriferous materials released during cooking are, however, strong air polluters and difficult to control.

Most kraft processors use coniferous woods, and the process deals readily with the large amounts of oil and resins in these woods. Most processes built during the last 10 years employ continuous digesters, although some large batch units are still being built. Batch units offer good control, but continuous units require less investment for a given capacity and make pollution control installation simpler and smaller. The trend has been toward very large units.

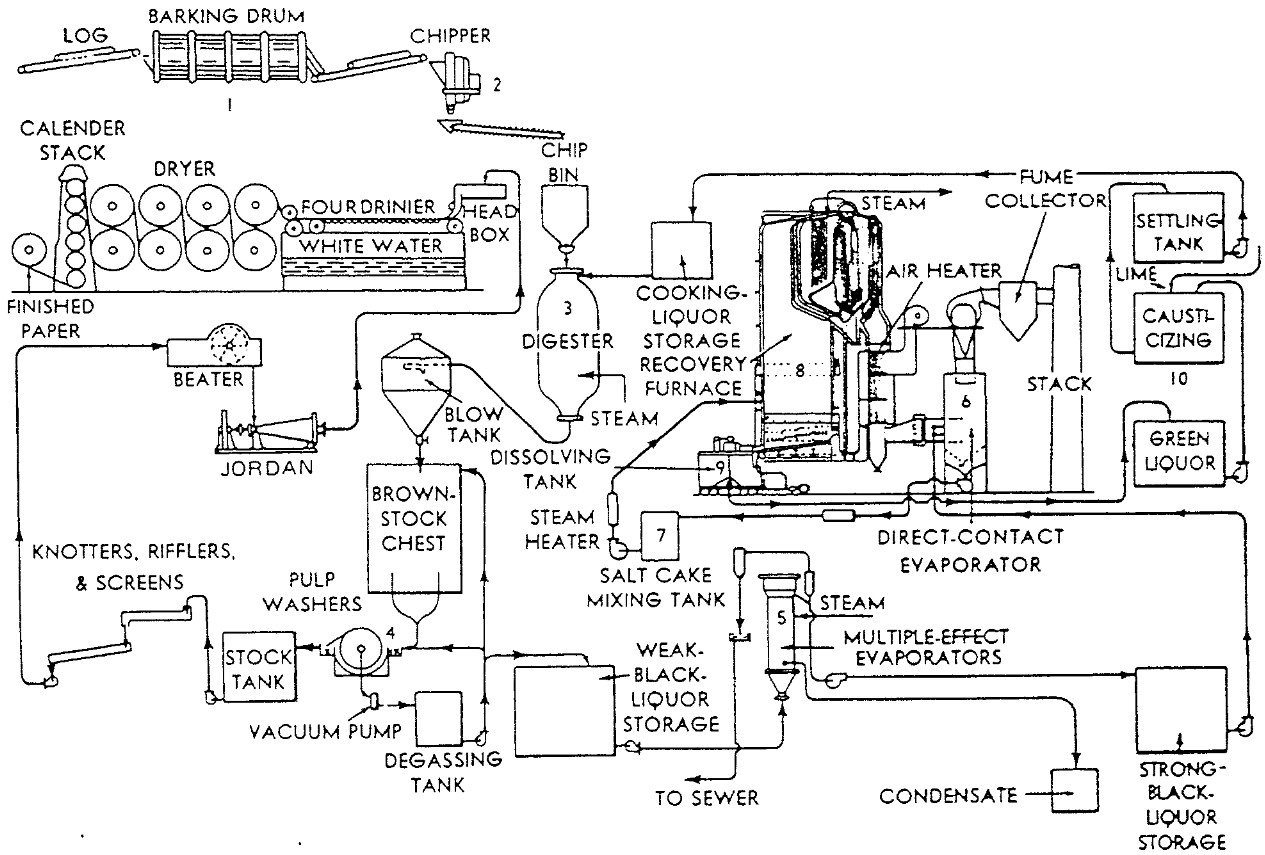
Figure 5.1 shows the overall kraft process including the important black liquor (processing chemical) recovery system. Table 5.3 summarizes the cooking conditions used for typical pulping procedures. Steam is usually recovered from the blow tank now, and the batch digester shown is generally replaced by a continuous one, the most popular unit being the Kamyr. A prehydrolysis step to remove pentosans and polyoses is common. The cooking process causes chemical reactions involving the hydrolysis and solubilization of the lignin, thus freeing the cellulose fibers. The turpentine is volatilized and sodium soaps are formed from the rosin acids. The hydrolysis frees mercaptans and organic sulfides which are the source of the foul odor associated with kraft mills.

When using a continuous digester, the manufacture of sulfate pulp involves the following sequences:

Logs are cut to convenient lengths and debarked as previously described, then conveyed to the chippers, which are large rotating disks holding four or more heavy knives. These reduce the wood to chips of preselected size

The chips are screened on either rotating or vibrating screens to separate the oversize chips, the desired product, and the sawdust. The oversize chips and slivers are sent to rechippers to reduce them to the proper size.

[4]Casey, *Pulp and Paper, Chemistry and Chemical Technology*, 3d ed., vol. 1, Wiley-Interscience, New York, 1980.




In order to produce 1 t of dried pulp, the following materials are required:

| | | | |
|---|---|---|---|
| Wood | 1.5–2 t | Steam | 6500 kg |
| New lime | 250 kg | Electricity | 900 MJ |
| Soda ash | 125 kg | Direct labor | 5.5 work-h |

Fig. 5.1. Flowchart for the kraft, or sulfate, pulping process with black-liquor recovery and reuse. Alkaline procedure. PROCESS NOTE: This flowchart is identical with one for the soda process, except sodium carbonate would be added instead of sodium sulfate (salt cake) *(Babcock and Wilcox Co.)*.

Chips enter the continuous digester and are presteamed at approximately 100 kPa, volatilizing the turpentine and noncondensable gases. They then pass to a higher-pressure impregnation zone at about 900 kPa, where their temperature is adjusted and they meet with the cooking liquor. Cooking time is about 1½ hours at 170°C. A quench flow of cold cooking liquor quickly stops the cooking reaction. Countercurrent displacement washing then reduces the chemical content of the chips, and the pressure is then reduced, producing flash steam which is used for the presteaming step on the entering chips.

The chips thus produced, along with their adhering liquor, are known as brown stock. Some method of heat recovery from this material usually precedes the washing step.

Pulp washing is an operation being aggressively studied now in hopes of reducing water use and simplifying water reclamation processes. High-density displacement washing is displacing the old repulping and straining procedures.

The spent cooking liquor, commonly called black liquor, is now ready to be treated to recover its chemical content for reuse and its organic content as heat. The black liquor recovery process is in many ways more difficult to run economically than the pulping process itself.

The washed pulp is passed over screens to remove knots, unreacted chips, slivers, trash, etc., then sent on to thickeners and filters.

The thickened pulp is next bleached, and here again, the technique is in a state of flux.[5] Chlorine and hypochlorite, the original materials used to oxidize and destroy the dyes and tannins of the wood, leave chloride residues in the wash water and harm the cellulose fibers. Chlorine dioxide is less damaging than $Cl_2$ or hypochlorite and is generally used in the first stage of a multiple-stage bleaching process. Bleaching is often done in dilute solutions followed by pulp concentration by dewatering and may use much water, contaminating all of it. Bleaching at high pulp consistencies is possible and highly desirable. Bleaching by reducing agents usually employs sodium dithionate $Na_2S_2O_4$, sodium borohydride, or bisulfite. Oxidative bleaches are ozone, $Na_2O_2$, $H_2O_2$, $ClO_2$, and chlorine.

After bleaching, the pulp is washed and rethickened in preparation for making it into coarse sheets dry enough to fold into a bundle, store, and ship—these are called laps. The pulp may also be used directly for making paper.

Laps are made on a wet thickener consisting of a suction cylinder dipping into a vat filled with fiber suspension. The cylinder discharges its load onto an endless felt belt which carries the pulp through squeeze rolls, then a series of press rolls. The resulting laps contain 35 to 45% air-dry fiber. The moisture is reduced further by stacking the laps in a hydraulic press and pressing them at around 20 MPa. The laps emerge with 50 to 60% air-dry fiber.

Kraft pulp, made from coniferous woods, has the longest fibers of all the pulps. This, coupled with the fact that the chemicals used are not so harsh in their action as those employed for other chemical pulps, makes possible the production of very strong papers. In the past, the dark color of kraft paper limited its use mainly to wrapping papers, sacks, and paperboard. Newer developments in the bleaching treatment have made possible the manufacture of light-colored and white pulps, allowing the mixing of this very high-strength pulp with other types to increase the paper strength.

*Recovery of the Black Liquor.*[6] An essential factor in the kraft process has been the recovery of the spent liquor from the cooking process. The black liquor removed from the pulp in the pulp washer, or diffuser, contains 95 to 98% of the total chemicals charged to the digester. Organic sulfur compounds are present in combination with sodium sulfide. Sodium carbonate is present, as are also small amounts of sodium sulfate, salt, silica, and traces of lime, iron oxide, alumina, and potash. Total solids usually average about 20%. This black liquor is concentrated, burned, and limed as shown in Fig. 5.1. In the smelting furnace any remaining organic compounds are broken down, the carbon burned away, and the inorganic chemicals melted. At the same time, the reaction

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

takes place. The carbon (reducing agent) comes from the organics in the wood.

The Thomlinson kraft recovery furnace is the unit presently most widely used for burning concentrated black liquor. Black liquor is concentrated to around 35% solids in multiple-effect evaporators, then the solution is sprayed directly into the Thomlinson furnace; there it is burned, the reduction of the sulfate to sulfide takes place, steam is made, and a molten salt mixture, or smelt, is produced. These complicated, often conflicting chores make adjustment and control of the furnace very difficult. A hazard exists because the molten smelt can cause

[5]Kohn, Pulp-Bleaching Process Cuts Costs, Time, Effluent, *Chem. Eng.* 54 (5) 136 (1977).

[6]Chase (ed.), *The Use and Processing of Renewable Resources*, AIChE Symposium Series 207, vol. 77, 1981.

explosions if it comes in contact with small amounts of water. Hydropyrolysis of dry black-liquor solids to produce combustible gases has been suggested, and fluidized-bed combustion of a 35% solution to produce chemical pellets instead of smelt has been tried. All the alternatives to the present system have some disadvantages and/or difficulties, but it seems probable that a more energy-efficient recovery system than the present one will shortly be forthcoming.

The molten chemical *smelt* is allowed to fall into a weak solution in tank 9 of the "dissolving liquor" coming from the causticizing plant. The chemicals dissolve immediately to give a characteristic green liquor. The insoluble impurities are allowed to settle out, and any carbonate is then causticized by adding slaked lime prepared from recovered calcium carbonate. The reaction

$$Na_2CO_3(aq) + Ca(OH)_2(s) \rightarrow 2NaOH(aq) + CaCO_3(s) \qquad \Delta H = -8.79 \text{ kJ}$$

occurs quickly. The resulting slurry is separated in settlers and rotary continuous filters, using Monel metal screens as a filtering medium. The calcium carbonate sludge, or "mud," is sent to a lime kiln to recover the calcium oxide for reuse in the process. The filtrate is the white liquor used in the cooking of the fibers. It contains sodium hydroxide, sodium sulfide, and small quantities of sodium carbonate, sodium sulfate, sodium sulfite, and thiosulfate.

Among the by-products from the black-liquor recovery plant is tall oil (Chap. 32), a black, sticky, viscous liquid composed mainly of resin and fatty acids. The tall oil may be separated from the weak black liquor by means of centrifuges (in America) or obtained by flotation from the concentrated liquors (in Europe). The digester relief gases yield paying quantities of turpentine, from 11 to 42 L per metric ton of pulp produced. This may be refined to produce sulfate turpentine.

***SODA PULPING.*** Soda pulping is brought about by a procedure similar to that used for sulfate pulp, except that the dissolving agent is $NaOH/Na_2CO_3$ and the make-up chemical is $Na_2CO_3$ instead of $Na_2SO_4$. Its importance is too small to warrant additional details here.

***SULFITE PULPING***

***Sulfite Pulp.*** The quantity of pulp made by this process steadily diminishes despite its high quality, because of the water pollution problems which it causes. Although spruce is the wood most commonly employed, appreciable quantities of hemlock and balsam are also used. The wood is barked, cleaned, and chipped as described for sulfate pulp, the resulting chips being about 1.5 cm in length. It is then conveyed to storage bins above the digesters preparatory to being cooked. The chemistry of the sulfite digestion of cellulosic materials is no more well understood than that of the sulfate process. Energy requirements are high. The usual sulfite process consists of digestion of the wood in an aqueous solution containing calcium bisulfite and an excess of sulfur dioxide. The sulfite process involves two principal types of reactions, which are probably concurrent: (1) sulfonation and solubilizing of lignin with the bisulfite, and (2) hydrolytic splitting of the cellulose-lignin complex. The hemicelluloses are also hydrolyzed to simpler compounds and the extraneous wood components acted on. Since disposal of waste liquor (more than half of the raw material entering the process appears here as dissolved organic solids) creates a serious water pollution problem, concerted attention has been turned to its removal or utilization. A slurry of magnesium oxide is substituted for lime,[7]

[7]Hull et al., Magnesia-Base Sulfite Pulping, *Ind. Eng. Chem.* 43 2424 (1951) (excellent article, flowcharts, pictures).

because then chemical and heat recovery are possible, and a solution to the disposal problem of the waste liquor is also provided. Sodium and ammonia[8] have also been substituted for calcium as a pulping base in a limited way. The waste liquor from the calcium sulfite process cannot have its values used over again, since the calcium sulfite does not decompose to sulfur dioxide, whereas magnesium sulfite does. $CaSO_4$ is formed and lost. Hence the newer and technically more acceptable[9] sulfite process is based on magnesium bisulfite rather than the earlier used, corresponding calcium compound, resulting in a greater concentration and more active combined sulfur dioxide, without danger of precipitation and with a quicker separation and solution of the noncellulose wood constituents (lignin and hemicelluloses) (Fig. 5.2).

The essential reactions involved in the preparation of the cooking liquor are quite simple:

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + H_2O + CaCO_3 \rightarrow Ca(HSO_3)_2 + CO_2$$

or

$$2SO_2 + H_2O + MgCO_3 \rightarrow Mg(HSO_3)_2 + CO_2$$

$$2SO_2 + Mg(OH)_2 \rightarrow Mg(HSO_3)_2$$

or

$$SO_2 + H_2O + NH_3 \rightarrow NH_4HSO_3$$

The entire process may be divided into the following sequences, as illustrated in Fig. 5.2 for the magnesium bisulfite process.

Sulfur is melted in a tank heated by the rotary burner and then fed to this burner for oxidation.

Any sulfur that is vaporized in the burner enters a combustion chamber, where it is oxidized to sulfur dioxide. The amount of air in this operation is closely controlled to prevent the formation of sulfur trioxide.

The sulfur dioxide obtained is cooled quickly in a horizontal, vertical, or pond cooler consisting of a system of pipes surrounded by water.

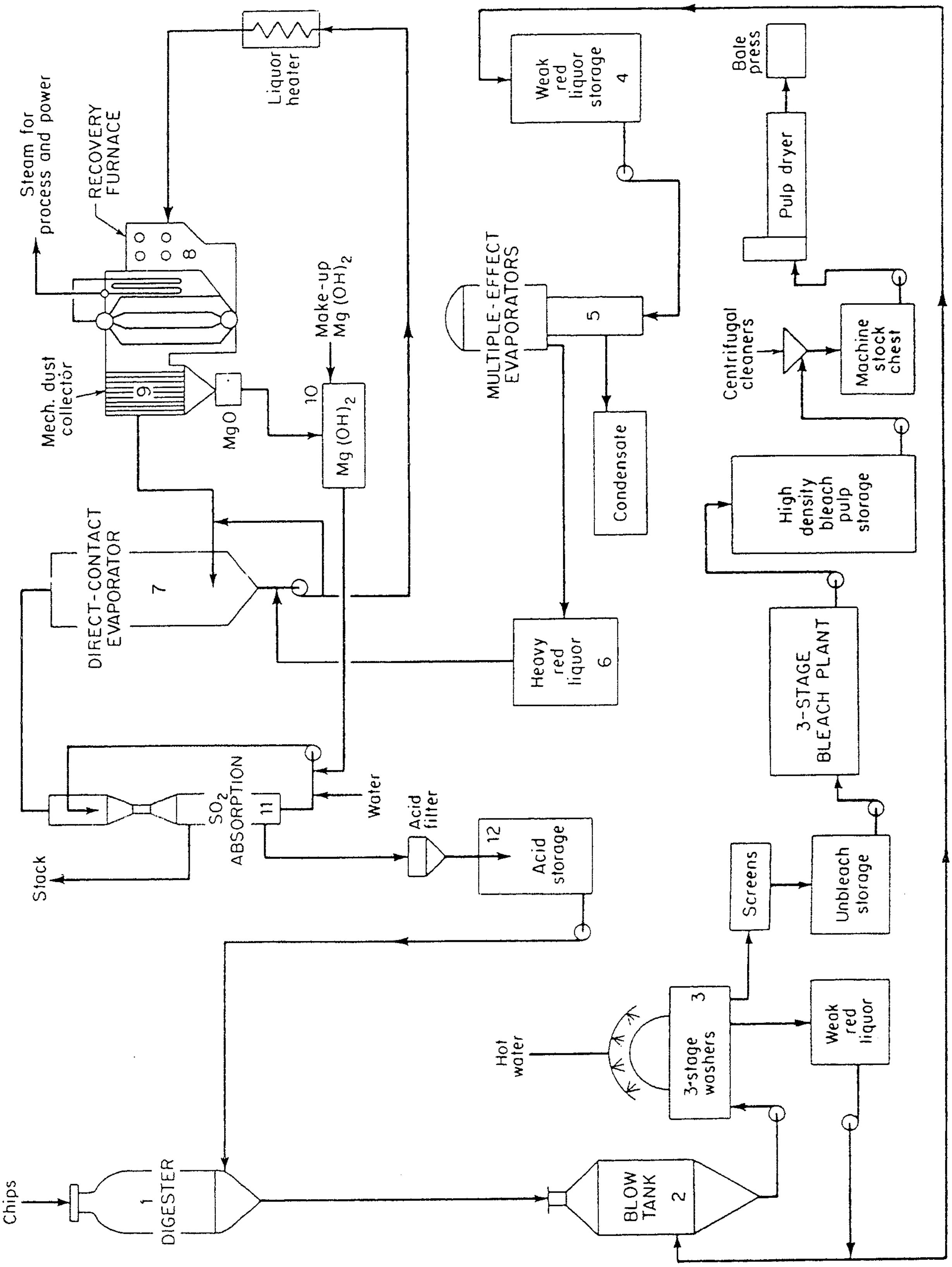
The absorption of the gas in water, in the presence of calcium, magnesium, or ammonium compounds, is accomplished in a series of two or more absorption towers or acid-making tanks

[8]Ammonia Base Sulfite Pulping at Inland Container, *Pap. Trade J.* November 20, 1972.

[9]Liquor-Making Eased for Mg-Base Pulp Mills, *Chem. Eng.* 71 (15), 80 (1964); It's a Big Job to Clean up Sulfite Waste, *Chem. Week.* **110** (17) 37 (1972); New Cleanup Methods Vie for Sulfite Pulping Jobs, *Chem. Week* **111** (17) 67 (1972).

| PULP GRADES | DISSOLVING | NEWSPRINT |
|---|---|---|
| Yield of pulp, % | 35 | 60 |
| Materials Consumed per Metric Ton, kg | | |
| Wood, oven dried | 2572 | 1500 |
| Magnesium oxide | 61 | 75 |
| Sulfur dioxide | 195 | 240 |
| Steam | 1450 | 1000 |
| Power, MJ | 14,526 | 10,026 |

Fig. 5.2. Flowchart of Magnefite pulping and magnesium oxide recovery. Improved acid sulfite pulping. *(Babcock and Wilcox Co.)*


Chips
1
DIGESTER
BLOW TANK
2
Hot water
3-stage washers
3
Weak red liquor
Screens
Unbleach storage
3-STAGE BLEACH PLANT
High density bleach pulp storage
Centrifugal cleaners
Machine stock chest
Pulp dryer
Bale press
Weak red liquor storage
4
MULTIPLE-EFFECT EVAPORATORS
5
Condensate
Heavy red liquor
6
DIRECT-CONTACT EVAPORATOR
7
Steam for process and power
RECOVERY FURNACE
8
Liquor heater
Mech. dust collector
9
MgO
10
$Mg(OH)_2$
Make-up $Mg(OH)_2$
Stack
$SO_2$ ABSORPTION
11
Water
Acid filter
12
Acid storage

for $Mg(HSO_3)_2$. A fine spray of the suspension passes down through the tower system countercurrent to the sulfur dioxide gas, which is blown up through the tower.

The liquor contains a certain amount of free sulfur dioxide, which is enhanced from time to time as the free sulfur dioxide vented from the digesters is bubbled through acid-making towers. The final liquor, as charged to the digesters, is a solution of calcium, magnesium, or ammonium bisulfites, analyzing about 4.5% "total" sulfur dioxide and about 3.5% "free"[10] sulfur dioxide. The digester is filled with chips, and the acid cooking liquor is pumped in at the bottom. The digesters are cylindrical steel vessels with a capacity of from 1 to 20 t of fiber and 10,000 to 200,000 L of "acid." A special acid-resisting lining is used to avoid the corrosive action of the cooking liquor.

The digester is heated with direct steam. In recent years the industry has turned to digesters with forced outside circulation, which heat the cooking liquor in an outside stainless-steel tube heater and circulate it through the charge by means of pumps. This permits better temperature distribution through the charge and prevents dilution of the liquor with the direct steam injection formerly used for heating. Conditions of the cook depend on the nature of the wood. the composition of the acid, and the quality of pulp charged. The pressure varies from 480 to 1100 kPa, depending upon the construction of the plant. The time and the temperature range from 6 to 12 h and from 170 to 176°C.

At the end of the cooking process the digester (1) is blown to a tank (2) a large, round tank having a false bottom and equipped with means to wash the pulp with fresh water. The cooking, or weak red liquor is evaporated (5–7) and burnt in a boiler (to provide steam) (8,9). MgO and sulfur dioxide are formed. The MgO is slaked (10) and pumped to the cooling and acid tower (11) down which the sulfur dioxide (regained and make-up) is passed to make fresh bisulfite liquor (12).

The pulp is pumped from the blow tank (2) to a series of screens (3), where knots and large lumps of fiber are removed. The accepted stock from the screens is sent to rifflers, or centrifuges, to remove foreign matter.

The relatively pure pulp is concentrated in thickeners, which are cylindrical frames covered with 80-mesh wire. The water passes through, and the pulp is retained on the screen.

The pulp is sent to the bleacher, where chlorine dioxide is introduced. After the chlorine has been exhausted, milk of lime is added to neutralize the mass.

The stock is washed, thickened and sent to the machine stock chest.

Pulp from the chest is formed into laps of about 35% dry-fiber content, and the laps are dried with steam-heated rolls in a pulp dryer and baled as a product which is 80 to 90% dry fiber.

The system of preparing the cooking liquor consists of slaking burnt lime containing a high percentage of magnesia with warm water to produce a 1°Bé suspension. This solution is treated with sulfur dioxide gas to produce the cooking liquor.

Sulfite pulp is a high-grade type of pulp and serves in the manufacture of some of the finest papers, including bond. It is used either alone or with some rag pulp to make writing paper and high-grade book paper. It furnishes dissolving pulps for plastics, synthetic fibers, and other products in which wood per se is unrecognizable.

It is easy to bleach, but the fibers are weak and the process began to be replaced as soon as the $ClO_2$ bleaching process made kraft bleaching practical.

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[10]In the parlance of the pulp manufacturer, the "free" sulfur dioxide is the sum of the sulfurous acid and that portion which requires alkali to convert from a bisulfite to a neutral sulfite.

*Waste Sulfite Liquor.* Calcium-based sulfite waste liquor does not permit recovery and reuse of either the Ca or S content. Magnesium- and ammonium-based liquor can be recovered simply, but the ammonia cannot be recovered. Sodium base can be recovered, but the recovery process is complex. Only the magnesium base is conveniently and simply handled, and this explains the reason why it is preferred. Until recently, it was common practice to use calcium base and simply dump the waste liquor into a nearby stream. A combination of public attention to water pollution and the necessity for recovering expensive chemicals has stopped this. Figure 5.2 shows the method for recovery and reuse of magnesia-based waste liquor. The dissolved organic matter is used to provide heat for the process.

Strong efforts to make better use of sulfite waste liquor than burning it have been made. Processes for recovering lignin; making vanillin from the lignin; and making tanning materials, road binders, portland cement accelerators, core binders, and food yeast have been developed.

***SEMICHEMICAL, OR NSSC, PULPING.*** Neutral sulfite semi-chemical (NSSC) pulping uses substantially less chemicals in pulping than the full chemical processes. The yield of pulp obtained from a given wood is, however, much higher. Most such pulps are used in linerboard and corrugating paper. Yields of pulp are as high as 65 to 80 percent, which makes for better use of the wood. Quality and bleachability are, of course, somewhat poorer. Continuous and batch digestors are both used. The idea is to make a mild cook weaken the binding material between the fibers, then separate them by mechanical means. Sodium sulfite buffered with sodium carbonate is the usual cooking medium, but other pulping agents, such as kraft green liquor can also be used, along with elevated temperatures to give enough softening to permit mechanical refining. The high yields obtained reduce stream pollution problems.

***MECHANICAL AND THERMOMECHANICAL PULPING.*** Stone-ground wood involves no chemical treatment. Soft coniferous species such as spruce and balsam are the chief woods employed. Debarked logs are held at an acute angle against a rotating stone so that the fibers will be torn apart rather than broken. Water is provided to remove the heat of friction and to carry the dislodged fibers away. "Pockets" around the face of the grindstone hold logs against it under pressure from hydraulic cylinders. The freed fibers are dropped into a container known as the stock sewer and passed along to a sliver screen. Here the fine material passes through into the stock pit and the coarser particles are separated and sent to some type of refiner, then returned to the screens. The fines are concentrated in thickeners, yielding mechanical pulp. The water overflow from the thickeners contains 15 to 20 percent of the original fiber and is recirculated to the grinders and used to facilitate flow in the stock sewers. As the process continues to operate, it is necessary to add fresh water to the system to keep the temperature down, so some white water must be removed. After straining out its valuable fibers, it is sent to waste. The only chemical change occurring during the process is a slight hydration of the cellulose due to its long contact with warm water.

Groundwood is used chiefly for cheaper grades of paper and board where permanency is not required. Chemical decomposition of the noncellulosic constituents sets in and results in eventual brittleness and discoloration. Mechanical pulp is rarely used alone. Even in the manufacture of newsprint, cheap Manila, wall, tissue, and wrapping papers, the mechanical pulp is usually mixed with a small amount of chemical pulp to add strength and improve color.

Groundwood pulp can be bleached, although not to the brightness of chemical pulp. Sodium and calcium bisulfites were the first bleaches used, but oxygen, ozone, chlorine dioxide, and sodium and hydrogen peroxide have proved to be more effective. Bleaching is an

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expensive process, as is any process consuming chemicals, and must be carefully designed to give the maximum brightness and fiber strength with a minimum of cost and degradation

Thermomechanical pulping takes advantage of the fact that elevated temperatures soften the lignin and make mechanical pulping less difficult The wood is steamed at around 975 kPa, and the refining is carried out at the high temperature (170°C) thus obtained The fiber obtained is coated with lignin and highly suitable for fiberboard, but makes poor paper

***NEW PULPING PROCESSES.*** Solvent pulping[11] with a variety of solvents such as ethanol, phenol, and other delignifying solvents that contain no sulfur continue to be suggested The holopulping process developed by the Institute of Paper Chemistry uses chlorine dioxide as a pulping agent. Straight oxygen and nitric acid pulping have also been suggested One of the more interesting ideas involves using anthraquinone in small quantity as a catalyst in ordinary pulping processes to speed them up. A few of these processes have reached the pilot plant stage, but paper companies show little inclination to gamble on risky new projects even when there are apparent savings in energy and the possibility of salable new by-products.

***SECONDARY FIBER PULPING.***[12] Over 20 percent of U.S. paper now comes from the repulping of recycled paper. There are a great many grades produced varying widely in quality. Batch processes are usually used. The collected material is repulped in water, cleansed of objectional dirt and contaminants, deinked with alkali [NaOH, $Na_2CO_3$, and $Na_2O(SiO_2)_x$], washed, cooked lightly with mild alkali, bleached, screened, then handled like any other pulp. Secondary fiber is worth about 5 times its value as waste paper. The largest single use is in the manufacture of multi-ply cylinder board. Here several sheets formed on a cylinder machine are combined to give a heavy paper. The outside layers may be virgin stock with the inside layers secondary fiber. Six major grades are generally recognized: chipboard, mill board, folding boxboard, combination Manila board, container board, and setup board. A continuous cooking process is also being used.

***RAG PULPING.*** The oldest material used for making paper, and the material still used for the finest grades, is cotton in the form of rags or cotton linters (the cotton fuzz adhering to cotton seeds after ginning). Old rags make pulp suitable only for felts, so clippings from textile manufacturing plants and clothing manufacturers are the major sources of raw material. Mixed fibers containing synthetics are undesirable, but rayon is quite suitable. Dyes can be removed with strong reducing agents. Rags must be chopped and cooked to remove sizing materials and then are treated in small batches in horizontal rotary cookers for 2 to 10 h at around 300 kPa. The rags are usually chipped into the short lengths needed for paper making before cooking. This business is quite small, and the equipment has not been much modernized. Paper made from rags has a much longer storage life than that made from wood fiber.

***DISSOLVING PULP.*** Where pulp is to be used for making cellulose derivatives, it is important that it be essentially pure α-cellulose.[13] Cotton linters are almost pure α-cellulose, but the

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[11] Katzen, Frederickson, and Brush, The Alcohol Pulping and Recovery Process, *Chem. Eng. Prog.* **76** (2) 62 (1980); Schweers, Phenol Pulping—A Potential Sulfur-Free Papermaking Process, *CHEMTECH* 4 (8) 490 (1974).

[12] Secondary Fiber Technology, *Tappi* 58 (4) 78 (1975); Paper Recyclers Regroup, *Chem. Eng.* **81** (12) 44 (1974).

[13] α-Cellulose is the technical term used in the trade. α-Cellulose is insoluble in an 18% NaOH solution after it is diluted. The standards for the test are available in ASTM publications

supply is not sufficient to meet the demand. Dissolving pulp is made by posttreatment of high-quality sulfite pulp with sodium hydroxide or from pre-hydrolyzed sulfate pulp. Such purified cellulose commands a premium price.

## MANUFACTURE OF PAPER

***WET PROCESS.*** The various pulps, even though frequently manufactured in coarse sheets, still lack those properties which are so desirable in a finished paper, such as proper surface, opacity, strength, and feel Pulp stock is prepared for formation into paper by two general processes, beating and refining. There is no sharp distinction between these two operations. Mills use either one or the other alone or both together. However, the beater is of decreasing importance with the increasing use of continuous refining. The operation of refining fits in well with the trend toward automatic mills.

The most generally used type of *beater* (also known as a Hollander, Fig. 5.3) consists of a wooden or metal tank having rounded ends and a partition part way down the middle, thus providing a channel around which the pulp circulates continuously. On one side is a roll equipped with knives or bars, and directly below this is a bedplate consisting of stationary bars. In operation, the circulating pulp is forced between the bars on the revolving roll and the stationary bars of the bedplate. The roll itself may be raised or lowered to achieve the results desired. Beating the fibers makes the paper stronger, more uniform, more dense, more opaque, and less porous. Bonding between fibers is increased by beating.

Most mills use some variation of the conical refiner, or Jordan engine (Figs. 5.4 and 5.5). Stationary bars of metal or stone are set inside the conical housing. The rotor is fitted with metal bars set to close clearance against the shell. Pulp enters the small end of the cone and passes out the other. The pulp is deformed, defibered, and dispersed, but not cut by the device.

Disk refiners perform similar duties by passing the pulp between rotating grooved disks.

In addition to fiber, paper also contains fillers, sizes, and frequently, dyes. These materials are generally added during the refining process. Various types of pulps are blended to give the desired properties, then the filler and color are added to the mixture and beaten to uniformity. Alum is then added to coat the fibers and coagulate the materials present. All papers except the absorbent ones (tissue, toweling, filter) require a filler to give a smoother surface, a more brilliant whiteness, improved smoothness and printability, and improved opacity. Fillers are always finely ground inorganic materials, usually naturally occurring substances such as talc or special clays or manufactured materials such as titanium dioxide, precipitated calcium carbonate, or certain silico-aluminates. The quantity of paper produced, by grades, is shown in Table 33.4.

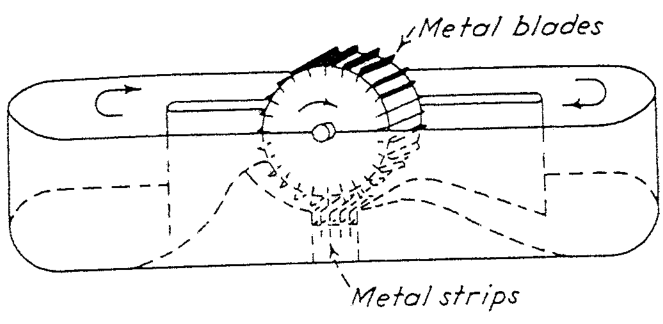


Fig. 5.3. Beater or Hollander.

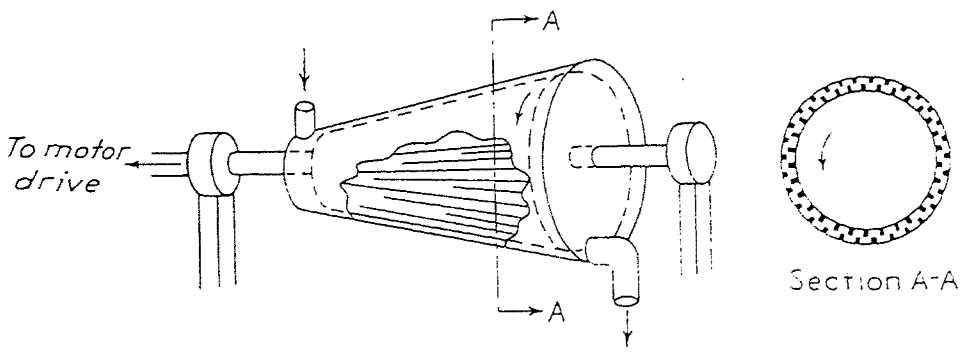


**Fig. 5.4.** Conical refiner or Jordan engine.

Sizing[14] is added to paper to improve resistance to penetration by liquids. Sizing may be added to the furnish (mixed pulp diluted and ready to add to the paper machine) or applied to the surface of the finished paper. Stock sizing involves adding size in the beater, then later precipitating it with papermaker's alum, $Al_2SO_4 \cdot 18H_2O$. The commonest sizing agent is rosin soap made from tall oil; wax emulsions are also used. Stock sizing forms a gelatinous film on the fiber which loses its water of hydration to produce a hardened surface. Tub sizing uses suitable solutions which, applied to the dried paper and calendered (ironed), produce a firm nonporous surface. Common tub sizes are modified starches and plastic materials. Such sizing is usually done on the dry end of the paper machine itself, but separate size presses are also used. The ability to take ink well, ink properly, resist moisture, and withstand erasure is all greatly improved by this process.

Conventional papers have wet strengths of less than 10 percent of their dry strength. Amino-aldehyde synthetic resins have been found to impart wet strength without causing water repellancy, and this has resulted in important additional uses for paper.[15]

Two types of conventional wet process paper machines are in use, the Fourdrinier machine

[14]Davison, The Sizing of Paper, *Tappi* 58 (3) 48 (1975) (a review)

[15]Thode et al., Mechanism of Retention of Wet Strength Resins, *Tappi* 42 (3) 178 (1959); 43 (10) 861 (1960); 44 (4) 290 (1961).

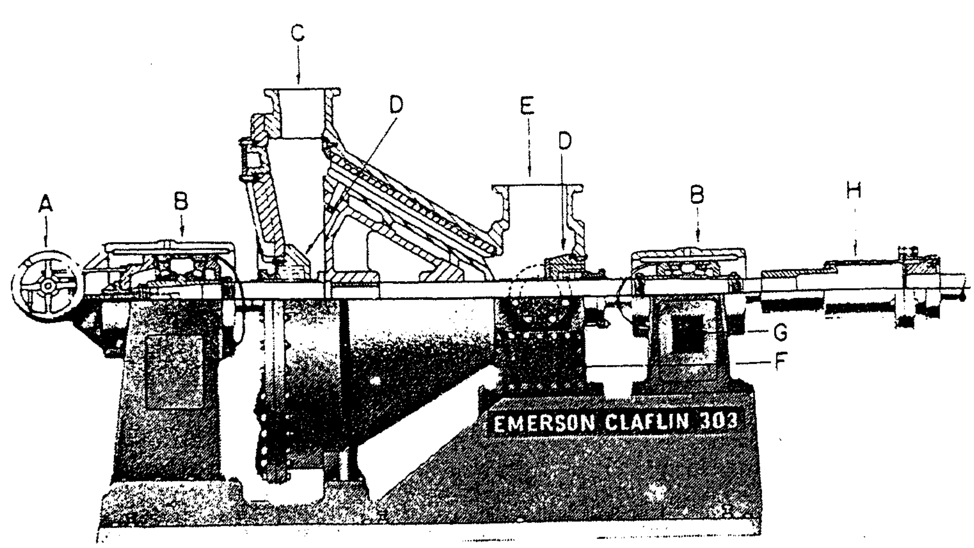


**Fig. 5.5.** Emerson Claflin refiner. (A) Plug adjustment mechanism, (B) bearing assemblies, (C) stock outlet, (D) packing boxes, (E) stock inlet, (F) cleanout, (G) oil-mist lubrication, (H) coupling, coupling. *(Emerson Mfg. Co.)*

***Table* 5.4** Paper and Paperboard Products, by Grades (in millions of metric tons)

| | 1975 | 1979 | 1980 |
|---|---|---|---|
| Paper and paperboard, all grades | 51.2 | 65.0 | 63.5 |
| Paper | 25.7 | 34.3 | 34.3 |
| Newsprint | 8.5 | 10.2 | 10.7 |
| Coated printing and converting | 2.8 | 4.2 | 4.3 |
| Uncoated book and other printing | 7.0 | 10.4 | 10.3 |
| Packaging and industrial converting | 3.9 | 5.4 | 5.1 |
| Tissue and other machine-creped | 3.5 | 4.1 | 3.9 |
| Paperboard | 21.2 | 26.4 | 24.9 |
| Unbleached kraft | 9.5 | 12.3 | 11.7 |
| Bleached fiber | 2.8 | 3.1 | 2.7 |
| Semichemical | 3.3 | 4.3 | 4.3 |
| Recycled furnish | 5.6 | 6.7 | 6.2 |
| Construction paper and board | 4.3 | 4.3 | 4.3 |

SOURCE: *Statistical Abstract of the United States,* 1981.

and the cylinder machine. Both form the paper by draining water from a dilute fiber mix through a fine screen and both dry the mat thus formed by dewatering with rollers, drying on heated rolls, and smoothing with calenders.

***FOURDRINIER MACHINE.*** Figure 5.6 shows the essential parts of a Fourdrinier machine. The very dilute stock from the foregoing operations, containing approximately ½% fiber, is first sent through screens to the head box from which it flows through a calibrated sluice onto a moving, endless wire screen. The pulp fibers remain on the screen, while a great portion of the water drains through. As the screen moves along, it has a sidewise shaking motion which serves to orient some of the fibers and to give better felting action and more strength to the sheet. While still on the screen, the paper passes over suction boxes to remove water and under a dandy roll which smooths the top sheet. Rubber deckle straps along the sides of the screen serve to form the edges of the paper.

From the wire, the paper is transferred to the first felt blanket, which carries it through a series of press rolls, where more water is removed and the paper given a watermark if so desired. Leaving the first felt, the paper passes through steel smoothing rolls and is picked up by the second felt, which carries it through a series of drying rolls heated internally by steam. The paper enters the rolls with a moisture content of 60 to 70% and leaves them 90 to 94%

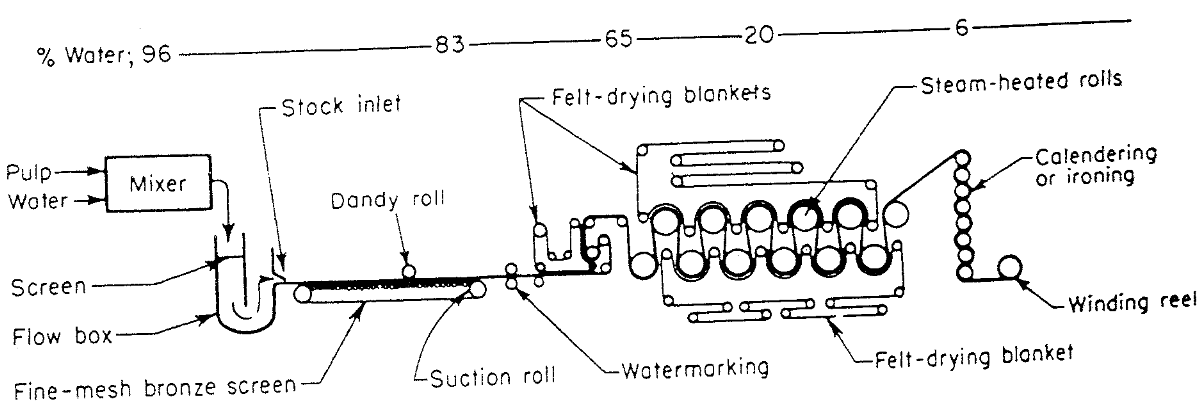


Fig. 5.6. Fourdrinier machine.

dry. Sizing may be applied on the sheet at this point, in which case it must pass through another series of drying rolls before entering the calender stack, which is a series of smooth, heavy, steel rolls which impart the final surface to the paper. The resulting product, finished paper, is wound on the reel. The enormous quantity of water used makes it necessary to recirculate as much of it as possible for economical operation. The operation of a Fourdrinier is a complex procedure. One of the major problems is making suitable allowance in the speed of the various rolls for the shrinkage of the paper as it dries. The operating speeds of the machine vary from 60 to 1800 m/s. The control of the temperatures, speeds, and consistencies of the parts of the paper machine is very complex, and had always been viewed as an art until computer control became available. Now computer control makes possible far less production of nonspecification paper; far fewer web breaks, which produce paper that must be rerun (broke); and faster and easier changing of one grade of paper to another. Computer control has been most satisfactory.

*Cylinder machines* are employed for the manufacture of heavy paper, cardboard, and nonuniform paper. The cylinder machine has from four to seven parallel vats, into each of which dilute paper stocks are charged. This allows several similar or dissimilar layers to be united in one heavy sheet. A wire-covered rotating cylinder dips into each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. As the cylinder continues to revolve, the paper stock reaches the top, where the wet layer comes in contact with and adheres to a moving felt. The traveling felt, carrying the wet sheet underneath, passes under a couch roll where some of the water is pressed out. This felt and paper come in contact with the top of the next cylinder and pick up another layer of wet paper. Thus a composite wet sheet or board is built up and passed through press rolls and on to the drying and smoothing rolls. Such a composite may have outside layers of good stock, whereas the inside ones may be of groundwood pulp.

A new process[16] combining the pressing and drying stages of the Fourdrinier, using hardwood pulp, and drying while under pressure has been disclosed. The process has been piloted at the U.S. Forest Products Laboratory in Madison, Wisc., and a commercial plant design is underway.

***DRY PROCESSES.*** Considerable interest in a dry process[17] for making paper and nonwoven fabrics exists because of the cost and complexity of drying equipment and the enormous process-water demands of conventional methods. Pilot plants have been built to make paper by dry processes, but there are difficult problems as yet unresolved.

***COATED PAPERS.*** Specialty papers are often coated with wax or plastic materials to impart special properties such as printability or resistance to fluids. Functional coatings are especially important for food products. The principal types of processes and equipment required for coatings are discussed in the Technical Association of the Pulp and Paper Industry Monographs.[18]

[16] A Cheaper Process for Making Better Paper, *Chem. Week* 129 (13) 24 (1981).

[17] Danish Firm Tests Dry Process for Paper, *Chem. Eng. News* 45 (6) 40 (1967); Sorenson, Analyzing the Use of High-Bulk Filters on Air Formed Paper/Non-woven Output, *Pap. Trade J.* **166** (11) 26 (1982).

[18] TAPPI Monograph Series (current literature available from TAPPI).